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Memorandum of Project MICHIGAN

TELLURIUM CRYSTAL GROWTH

R. C. KEEZER



INFRARED LABORATORY

Institute of Science and Technology
THE UNIVERSITY OF MICHIGAN

December 1963

Contract DA-36-039 SC-78801

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NOTICES

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PREFACE

Project MICHIGAN is a continuing long-range research and development program for advancing the Army's combat surveillance and target-acquisition capabilities. The program is carried out by a full-time staff of specialists in physics, engineering, mathematics, and psychology at the Institute of Science and Technology, and by members of the teaching faculty and graduate students of other research groups and laboratories of The University of Michigan.

The emphasis of the Project is upon research and imaging radar, MTI radar, infrared, radio location, image processing, and special investigations. Particular attention is given to all-weather, long-range, high-resolution sensory and location techniques.

Project MICHIGAN was established by the U. S. Army Signal Corps at The University of Michigan in 1953 and has received continuing support from the U. S. Army. The Project constitutes a major portion of the diversified program of research conducted by the Institute of Science and Technology in order to make available to government and industry the resources of The University of Michigan and to broaden the educational opportunities for students in the scientific and engineering disciplines.

Documents issued in this series of Technical Memorandums are published by the Institute of Science and Technology in order to disseminate scientific and engineering information as speedily and as widely as possible. The work reported may be incomplete, but it is considered to be useful, interesting, or suggestive enough to warrant this early publication. Any conclusions are tentative, of course. Also included in this series are reports of work in progress which will later be combined with other materials to form a more comprehensive contribution in the field.

Progress and results described in reports are continually reassessed by Project MICHIGAN. Comments and suggestions from readers are invited.

Robert L. Hess
Director
Project MICHIGAN

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TELLURIUM CRYSTAL GROWTH

ABSTRACT

Techniques employed for the preparation of single crystal tellurium by the slow-cooling vapor, Bridgman, and Czochralski methods are described; the last method is emphasized. The Czochralski method has provided large (17 mm diameter by 70 mm long) single crystal boules, and lends itself to the addition of dopants during crystal growth. The ready cleavage parallel to the c axis evidenced by tellurium crystals requires the use of special techniques for fabrication of samples for optical and electrical evaluation.

INTRODUCTION

1.1. PREVIOUS WORK

Results obtained in the Infrared Laboratory in July 1957 indicated that single-crystal tellurium could be used as an intrinsic photoconductive detector of infrared radiation. It was noted [1] that single-crystal tellurium detectors have good sensitivities and short response times. These characteristics make them suitable for use in two-color infrared scanning systems, for scanning systems which use matched linear arrays of detectors, and for infrared sensors which operate under conditions of high atmospheric attenuation.

The single crystals used for evaluation were small prisms with hexagonal cross sections. These crystals, grown by sublimation, were 1 mm to 4 mm long and 0.1 mm to 1.0 mm wide.

More recent work in this laboratory indicates that doping the tellurium with small amounts of certain other elements (such as selenium, sulphur or arsenic) improves the sensitivity and decreases the response time of the resulting detector. The doping was accomplished by growing the crystals from tellurium vapor in an atmosphere of selenium, sulphur, or arsenic. The resulting crystals, however, have a tendency to be nonuniform in their impurity concentration; there may be an impurity gradient within a given crystal, and separate crystals would have different impurity concentrations. Moreover, there is no theoretical explanation available which adequately describes the vapor-phase doping phenomenon, so that the experiments become time consuming, the yield is low, and it is difficult to predetermine the amount of the added dopant element that finds its way into the crystal lattice.

It was decided that a more satisfactory method for producing large single crystals of tellurium was needed. The process of pulling a single crystal from the melt (the Czochralski method [2]) appeared most promising. This technique had been used successfully in the Infra-red Laboratory for the preparation of single crystals of such materials as germanium, antimony, sodium chloride, potassium chloride, and indium antimonide. This method also permits the addition to the growing crystal of controlled quantities of foreign elements that may modify the properties of the resulting tellurium detectors.

Uniform single crystals of tellurium 17 mm in diameter and 70 mm long, have been grown by the Czochralski method (see Figure 1). Resistivity and Hall measurements indicate that these undoped crystals have a carrier concentration of about 10^{14} per cubic centimeter. They are free from microscopic voids or "blowholes" and other macroscopic crystalline imperfections.

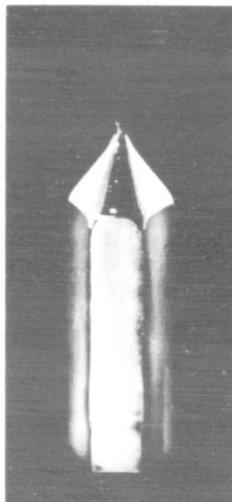


FIGURE 1. CZOCHRALSKI-GROWN TELLURIUM CRYSTAL

1.2. PROPERTIES OF TELLURIUM

The crystal structure of tellurium consists of parallel spiral chains of tellurium atoms terminating at the corners and center of a regular hexagon. The primitive unit cell contains three adjacent atoms in a chain so that the end projection of a chain is an equilateral triangle. Adjacent atoms in a chain are all spaced 2.86 Å from center to center. The second nearest neighbors are in adjacent chains and are 3.46 Å apart. From these two distances we expect atoms

along a chain to be bonded more strongly than atoms of adjacent chains. It happens that the bonding between chains is so weak that the material has perfect cleavage parallel to any face of the hexagonal prism. Figure 2 shows the arrangement of the atoms in tellurium.

Since the structure of tellurium is most easily visualized on a hexagonal basis, it is sometimes considered a hexagonal material. However, X-ray Laue photographs do not show the six-fold symmetry characteristic of hexagonal structures, but indicate instead a threefold symmetry resulting from the threefold screw axis. Tellurium has D_3 point symmetry and belongs to the trigonal class. The space group of tellurium may be D_{3d}^4 or D_{3d}^6 , depending on which way the atoms in a spiral rotate. This results in "mirror-image" or enantiomorphous crystals. On the basis of its crystal structure, one expects tellurium to be optically active and piezoelectric. Optical activity has been observed [3] but no report has been made of a piezoelectric effect in tellurium. We should also expect that many physical, optical, and electrical properties of tellurium should be anisotropic because of the anisotropic crystallography. Of importance for crystal growth is the fact that the thermal coefficient of expansion and thermal conductivity are highly anisotropic. The thermal coefficient of expansion is negative parallel to the c axis.

Table I gives some of the properties of tellurium which are important in crystal growth.

TABLE I. PROPERTIES OF TELLURIUM

Melting point	723°K
Boiling point	1663°K
Vapor pressure at 725°K	0.24 mm Hg
Latent heat of fusion	4.2 kcal/mole
Molar heat capacity (solid)	$4.46 + 0.00546T$ cal/deg per mole
Molar heat capacity (liquid)	9.0 cal/deg per mole
Density	6.28 g/cm ³
Thermal conductivity	0.015 cal/cm sec deg at 300°K
Atomic weight	127.61 g/mole
Volume increase on melting	~2%
Hardness (moh)	~2.5

(Smithells, Colin, Metals Reference Book, Interscience Publishers, Incorporated, New York, 1955)

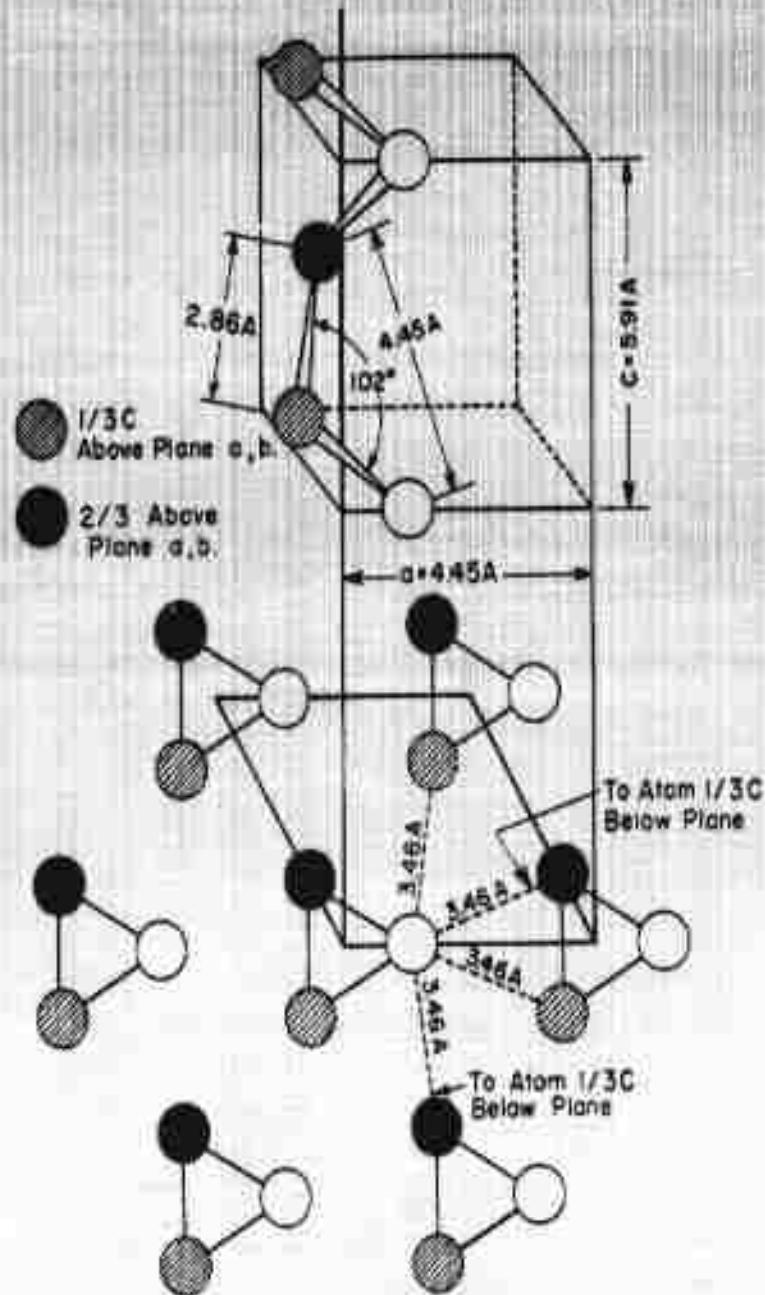


FIGURE 2. STRUCTURE OF HEXAGONAL TELLURIUM (David Leslie Waldorf, Preparation of Tellurium Single Crystal, MS Thesis, Purdue University, January 1957)

2
MATERIAL PURIFICATION

Although elemental tellurium is sometimes found in nature in the form of small hexagonal prisms, most commercial tellurium is obtained as a by-product from the processing of silver, gold, and copper.

The material used in this study was obtained from the American Smelting and Refining Company. Table I presents the spectrographic analysis results which were supplied with this material. The starting material was always very badly oxidized, as evidenced by a gray or purple surface. Table III presents the results of spectrographic analyses of several single crystals of tellurium which were grown in the infrared laboratory by the Czochralski method (see Section 3.5).

TABLE II. SPECTROGRAPHIC ANALYSIS OF SPECIAL HIGH-PURITY TELLURIUM. Provided by American Smelting and Refining Company

ELEMENT	PERCENT FOUND
Antimony	ND
Thallium	ND
Magnesium	<0.0001
Manganese	ND
Lead	ND
Tin	ND
Silicon	<0.0001
Chromium	ND
Iron	<0.0001
Nickel	ND
Bismuth	ND
Aluminum	ND
Calcium	ND
Copper	<0.0001
Indium	ND
Cadmium	ND
Zinc	ND
Silver	ND
Arsenic	ND
Mercury	ND
Tellurium	99.999% by difference

(ND indicates "none detected" by standard spectrographic methods)

**TABLE III. SPECTROGRAPHIC ANALYSIS OF
SINGLE-CRYSTAL TELLURIUM**

ELEMENT	PERCENT FOUND		
	SAMPLE 5	SAMPLE 6	SAMPLE 112
Magnesium	<0.00005	<0.00005	<0.00005
Silicon	<0.00006	<0.00005	<0.00005
Selenium	<0.0001	<0.0001	<0.0001
Iron	<0.00004	<0.00004	<0.00004
Boron	<0.0001	<0.0001	<0.0001
Germanium	ND	ND	ND
Lithium	ND	ND	ND
Lead	<0.00005	<0.00005	<0.00005
Tin	<0.00005	<0.00005	<0.00005
Copper	<0.0001	<0.0001	<0.0001
Chromium	<0.0001	<0.0001	<0.0001
Bismuth	ND	ND	ND
Beryllium	ND	ND	ND

(ND indicates none detected)

Halogens, sulfur, and selenium are not usually determined spectrographically. However, close examination on several lines indicates these nonmetals less than 1 ppm. Boron is the only element of the group listed whose intensity came near being as bright as 1 ppm.

Tellurium is more easily oxidized than iron and more difficult to oxidize than zinc. The known oxides are TeO , TeO_2 , and TeO_3 . TeO and TeO_3 decompose readily to form TeO_2 and Te . Tellurium dioxide is quite stable and forms white or yellowish crystals which float on molten tellurium. TeO_2 decomposes somewhat at about 450°C , but apparently the decomposition is relatively slow below 500°C . Simple vacuum distillation is not effective in removing the oxides, since they decompose at the melting point and reform upon condensation. Distillation in a hydrogen atmosphere is somewhat effective in removing the oxides. Reduction with hydrogen is not simple since the reaction products include H_2Te along with traces of water. Separation of these materials is difficult. Most of the oxides may be removed by draining molten tellurium through small holes in a carbon or quartz crucible. The tellurium is then distilled in a hydrogen atmosphere.

After the oxides have been removed, the material is further purified by vacuum distillation. This technique is very effective because of the large difference of the vapor pressure of tellurium and common impurity elements. Our apparatus is a long glass tube with three temperature zones. The molten tellurium (at 460°C) is at one end. Tellurium and volatile impurities vaporize, and the tellurium condenses at the center of the tube at about 440°C . The volatile

impurities are either condensed at the cool end of the tube ($\sim 100^{\circ}\text{C}$) or pumped out by the vacuum pump into a liquid-nitrogen trap. The impurities with low vapor pressures are left in the hot section where the tellurium vaporizes.

Weidel [4] reports another method of purification: H_2Te is produced by electrolysis and thermally decomposed to pure tellurium.

After the material has been distilled, it is placed in a Vycor crucible in the pulling apparatus. When the material is melted, some impurity occasionally forms a grey or black powder on the surface of the melt. We suspect this to be carbon, an oxide, or an amorphous form of tellurium. A black amorphous form of tellurium has been reported many times, but little is known about its properties. This powder is removed by lowering a seed to the melt and solidifying the surface of the melt. The cap is then withdrawn and removed from the apparatus. The resulting melt is completely free of any observable impurities and can be cooled at least 30°C below the melting point of tellurium before solidification takes place. Solidification may be affected by tapping or disturbing the pulling apparatus. Solidification is by means of dendritic growth, the rapidity of which depends on the degree of subcooling. Under ideal conditions, solidification of the entire melt has taken place with three observers unable to see any nucleation.

Weidel [4] reports that zone refining did not alter the conductivity of tellurium. However, Blakemore et al. [5] have reported that zone refining increases the carrier lifetime.

Shvartsenau [6] reports results of zone refining tellurium with up to nine passes of the molten zone. He reports purity greater than 99.9999%. Our experience indicates that the zone refining of tellurium results in no change in the conductivity and that, because of the high vapor pressure of tellurium, improvement by zone refining of commercially available 99.99% pure tellurium is much more difficult than improvement by vacuum distillation. It should be noted that when single crystals are prepared by the Czochralski technique, the material is effectively zone refined to the extent of one pass. Since the distribution coefficients for impurities in tellurium are not known, we do not know to what extent this one pass can benefit the material.

3 CRYSTAL GROWTH

Single crystals of tellurium have been prepared by the Czochralski method [4, 7, 8], by the Bridgman technique [9], by condensation from the vapor [1], and by zone melting [10]. No reports on crystal growth by the floating-zone technique, crystallization from solutions, hydrothermal techniques, or electro-deposition are known.

The Czochralski crystals have been prepared with carrier concentrations of less than $10^{14}/\text{cm}^3$ and etch-pit densities as low as $10^3/\text{cm}^2$. These crystals have been used to measure many of the electrical and optical properties of tellurium.

Tellurium has been doped with antimony and bismuth, the halogens [11], and tellurium [12]. We have doped tellurium with selenium, sulfur, phosphorous, arsenic, and silver. Very little is known about the solubility of impurities in tellurium. Weidel [4] reports a distribution coefficient of 1/2 for antimony in tellurium.

3.1. SLOW COOLING

Bottom [13] has reported the use of slow cooling to produce single-crystal tellurium. A Pyrex tube, filled with tellurium and helium, was suspended in molten KNO_3 . It was found that if the ID of the tube was 6 mm or less, single crystals were formed on cooling.

We have prepared single crystals by slowly cooling molten tellurium in a hydrogen atmosphere. Pure material was placed in a shallow 20-cm³ quartz crucible. The material was heated by a resistance heater until melted and then allowed to cool slowly. Solidification took place from the top down. The ingot thus formed was removed and broken. It was found that the crystal grain size was 5 to 10 mm on one edge. Some triangular prisms were cleaved from these grains. Several crystals with perfect cleavage were obtained. These prisms were subsequently used as seeds for the growth of larger crystals by the Czochralski method (see Section 3.6).

3.2. BRIDGMAN TECHNIQUE

Caldwell [9] has reported growing single crystals of tellurium by lowering a tube of molten tellurium through a temperature gradient in such a way that solidification takes place from the bottom upward. This, basically, is the vertical Bridgman technique. It was found that, even for tapered tubes, the maximum inside diameter for single-crystal growth was 6 mm.

We have observed crystal growth during zone purification in what is essentially a horizontal Bridgman apparatus. A molten zone is passed along a slender boat filled with tellurium. Crystals are usually in the form of rods several cm long and a few mm in diameter. No attempt was made to perfect this method.

3.3. VAPOR GROWTH

The technique used by the Infrared Laboratory for vapor growth of tellurium crystals was used by Suits [1] during vacuum distillation of tellurium. The equipment consists of a Pyrex

tube about two feet long surrounded by a resistance heater. The heater is wound so as to produce a temperature gradient along the length of the tube and is constructed as shown in Figure 3. Kanthal resistance wire, B, is wound onto a ceramic tube, A. The spacing between turns is small at the hot section and is gradually increased until the cool section is reached. Alundum cement, C, in the form of a paste, is applied over the windings and allowed to air dry. Several layers of asbestos, D, are applied over the alundum cement. Small thermocouple holes, E, are drilled between the windings. The heater is dried by operating for several days at a low temperature.

A vacuum pump is connected to one end of the tube, which extends about six inches out of the heater. Tellurium is placed in the hot portion of the tube, and vapors condense along the cooler length of the tube.

Figure 3 shows several regions in the tube where tellurium is deposited. In region F, a black deposit of amorphous tellurium is formed. Adjacent to the amorphous material is a deposit, G, of tellurium which is very thin and gives the appearance of a silvered mirror. Needle-like crystals grow in regions H, J, and K. The crystals in region H are less than 1 mm on an edge and densely packed together. The crystals in regions J and K are not closely packed and are much longer than those in regions H. Region L is a portion of the tube which is at a temperature above the melting point of tellurium but is still cooler than the molten material in region M. Liquid drops therefore form in region L.

More than a hundred runs have been performed with various modifications of this technique. Crystals about a millimeter in diameter and a centimeter in length are common. The largest crystal produced by this method grew along the wall of the tube and had three perfect faces of the hexagonal prism. This crystal was 4.7 cm long and 7 mm in diameter.

Crystals usually grow in the shape of hexagonal prisms with the base of the prism attached to the wall of the Pyrex tube. The smaller crystals grow perpendicular to the wall of the tube, and the larger crystals usually grow at an acute angle to the wall toward the hot section.

The larger crystals were grown in a closed tube. The tube, with tellurium in it, was evacuated to about 10^{-5} mm of Hg and then filled with hydrogen gas. This was repeated several times. Finally, hydrogen was admitted and the tube was sealed off. The effect of hydrogen gas on the crystal growth was investigated. We found that, with our apparatus, the largest crystals were obtained with an initial hydrogen pressure of about 10^{-1} mm of Hg, and that the growth rate slowed down as the hydrogen pressure increased. The effect of hydrogen is to slow down the transport of tellurium vapor from the hot section to the cool section. It is also quite probable that hydrogen gas transports heat, via convection, from the growing crystal.

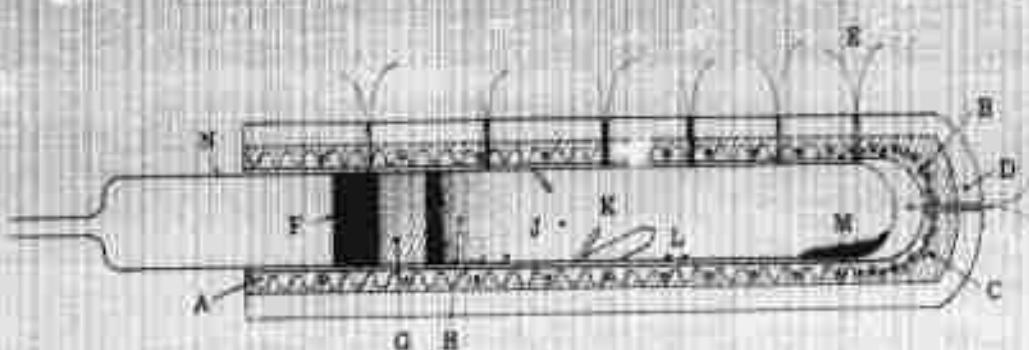


FIGURE 3. VAPOR GROWTH OF TELLURIUM CRYSTALS. A, Ceramic Tube; B, Kanthal Wire; C, Alundum Cement; D, Asbestos; E, Thermocouple Holes; F, Amorphous Tellurium Region; G, Tellurium Mirror Region; H, J, K, Crystallization Region; L, Liquid-drop Region; M, Molten Region; N, Pyrex Tube

Crystals grow at different rates along the length of the tube. Crystals in the hotter regions J and K (see Figure 3) grew at the rate of 1 cm per day; the growth rate, however, was not uniform. Nucleation in region K does not occur for up to 10 hours. Growth proceeds rapidly for 10 to 20 hours until the crystals grow into region L. Liquid drops will then form on the ends of the crystals.

The entire Pyrex tube is gradually pulled out of the heater to permit continued crystal growth in region K. This was done discontinuously—i.e., approximately 2 mm every hour. Eventually smaller crystals start to grow around the base of the larger crystals. Unless the process is modified, therefore, the size of the crystals in the K region is limited.

As the tube is withdrawn, the liquid drops in the L region solidify and become nucleation sites for new crystals. These crystals may interfere with the growth of larger crystals in the K region.

Hollow crystals of tellurium have been grown by sublimation. Figure 4 is a photomicrograph of such a crystal in cross section. These crystals were always formed in a region where the temperature gradient in the substrate was large.

A Pyrex tube 25 mm in diameter was placed in a tube heater one foot long and held at a temperature of 500°C. The tube extended six inches out of the heater; this caused a large temperature drop near the point where the tube entered the heater. Hollow crystals were formed by sublimation in this region of drastic temperature change. The crystals were usually in the shape of hexagonal needles, one or two centimeters in length and from 0.1 to 2 mm in diameter. The wall thickness was always small, about 0.01 to 0.1 mm. No variation in wall thickness was observed along the length of the crystals. This was determined by breaking the crystals at several points along their length.

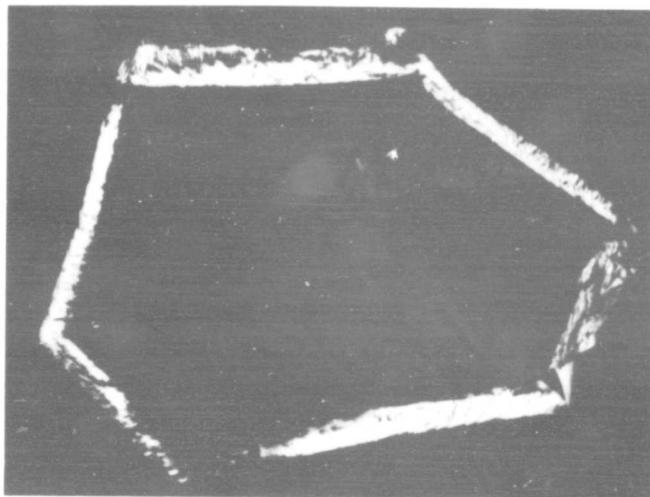


FIGURE 4. CROSS SECTION OF HOLLOW TELLURIUM CRYSTALS

Hollow plates 1 mm thick by 3 mm by 5 mm were also grown under the same conditions as were the needles. All hollow crystals grew very rapidly. Needles one to two centimeters long grew in three hours from the cool base toward the hot section. Growth appeared to start on a solidified liquid drop from which several needles would then grow rapidly. Platelets would then grow radially from this drop, nucleating on the needle and growing perpendicular to it. Usually one face of the plate was not complete. All faces of the hexagonal needles were complete except for some of the crystals larger than one millimeter in diameter.

Very little is known about hollow crystal growth. It is probable that the crystal nucleates at a screw dislocation site on the solidified liquid drop. Several conditions thought to encourage the growth of hollow crystals are present during the growth of these needles. The thermal conductivity of tellurium is greater parallel to the c axis than perpendicular to it. This encourages the crystal to grow in the form of slender needles with the heat flowing down the c axis to the cool base. A large temperature difference at the base of the crystal enhances this effect.

Screw dislocations have been used to explain rapid growth of crystals. The nature of growth via a screw dislocation is compatible with, and may even enhance, hollow crystal growth. Once any concave surface was formed on the tip of growing crystal, tellurium vapor would have to

diffuse into this concave area in order for growth to occur at the center of the tip. The concentration of tellurium vapor within the concavity would therefore be less than the concentration of tellurium vapor surrounding the surface. This should encourage the surface to grow faster than the bulk and make the concave hole even deeper. Once this condition is reached, one should observe only hollow crystal growth.

This last argument is supported by the incomplete faces on the larger crystals. It is likely that the side of the crystal facing the vapor source would grow completely whereas the back face would be shielded from the vapor source and therefore would not grow as rapidly as the front face.

Figure 5 illustrates another apparatus which was used in the vapor growth of tellurium crystals. The upper bulb is a one-liter flask. Two heaters were constructed so that tellurium could be vaporized in the lower section and allowed to condense within the Pyrex bulb. A "cold finger" with cool air impinging on its tip concentrates the growth in a small area. The crystal growth can be observed through a small port in the large heater.

The apparatus was designed to allow the crystals to grow toward the vapor source without wall interference. The crystal growth rate may be varied by adjusting the temperature and flow rate of the air impinging on the tip of the cold finger. Eleven runs were made with this apparatus; needle growth was never observed nor were hollow crystals formed. However, this may be because no runs were made with the cold finger cooled drastically.

Growth on the end of the cold finger took place as follows. During the first hour, very small crystals were formed. At low cooling rates, these crystals continued to grow with the c axis parallel to the walls of the cold finger. At the same time crystals start to form in isolated spots on the walls of the bulb. Growth is slow (about 1 mm^3 per day).

The temperature of the large heater may be increased so that nucleation will not occur on the walls of the bulb. An increase in the air flow is then necessary for crystal growth on the cold finger. Under these conditions, a large number of nuclei appear on the tip of the cold finger: a solid layer then forms, from which larger crystals grow. Crystals 3 mm across and 5 mm long were grown in two days under these conditions.

None of the vapor-grown crystals showed signs of layer-type growth, and the faces were always planar. Both right- and left-handed crystals were observed. Branching was never observed except for the platelets described earlier. Work on this technique was discontinued in order to concentrate on the growth of tellurium crystals from the melt.

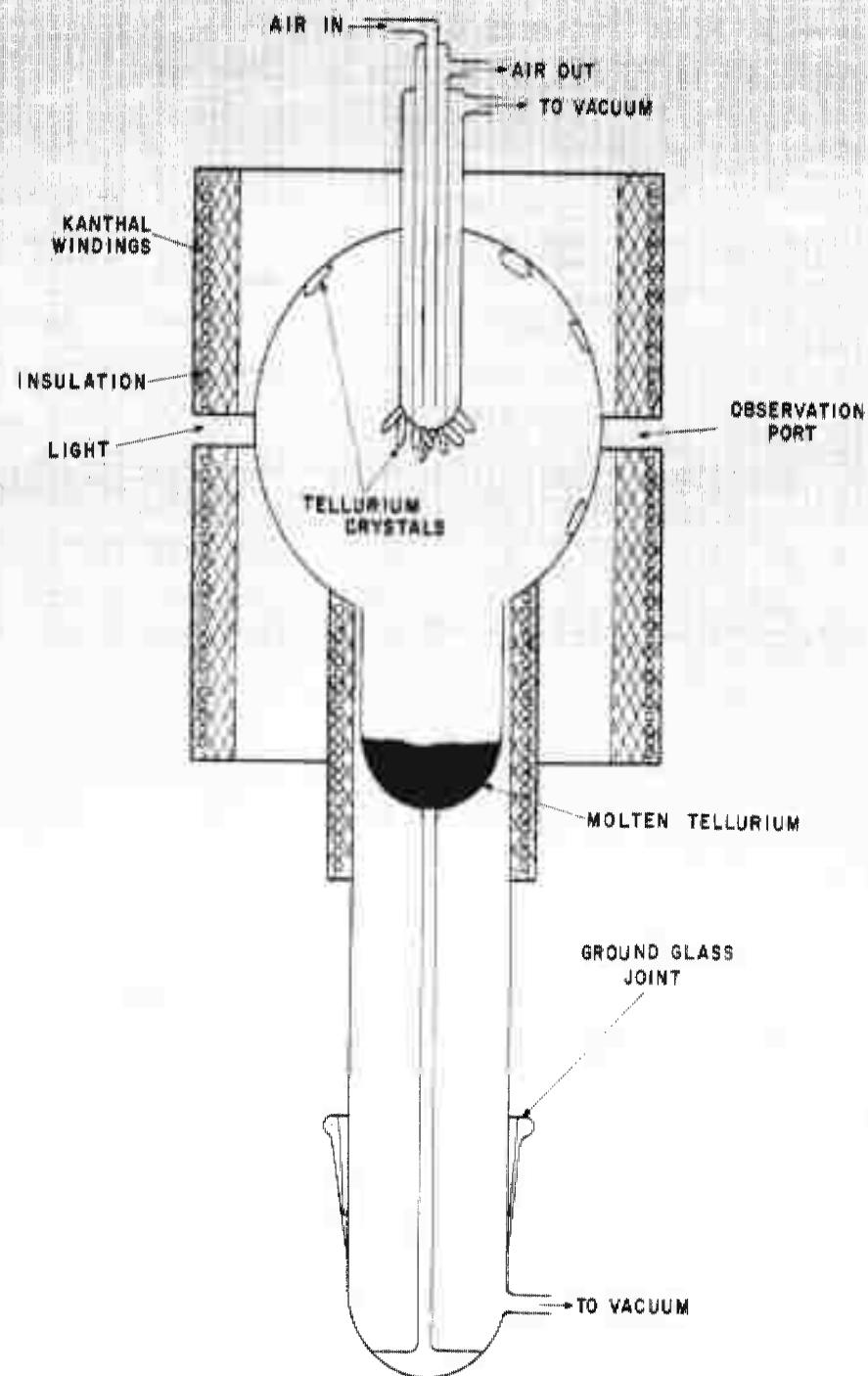


FIGURE 5. VAPOR GROWTH APPARATUS

Both needles and plates of tellurium formed on the walls of the Czochralski pulling apparatus (see Section 3.6). These were always hollow and were identical in appearance to the hollow crystals grown in the tube furnace.

3.4. RECRYSTALLIZATION

An evacuated tube containing small crystals of tellurium was placed in a tube furnace at 420°C. This tube had no cool sections. After one week, the tube was cooled slowly and removed. The small crystals had grown together and recrystallization had taken place. The original crystal had increased in size from an average of 1 mm³ to an average size of 10 mm³. Crystals in the shape of hexagonal prisms started to grow radially from the surface. All of this growth had taken place where the original crystals were placed.

It seems likely that some of the mass transport had taken place through the vapor and that sublimation took place with the original crystals acting as nuclei. Some recrystallization had probably taken place also by self diffusion from one crystallite to the other, since the largest crystals were over 100 mm³ and would not have reached this size without encountering smaller crystals with a different orientation of the crystallographic axis.

3.5. DENDRITIC GROWTH

Figure 6 is a photo-micrograph of tellurium dendrites obtained by seeding a subcooled melt and then rapidly withdrawing the seed. Figure 6 also shows dendrites formed by allowing the surface of a molten bath of tellurium to solidify and then rapidly withdrawing the entire surface from the subcooled melt. It can be seen that typical dendritic growth had taken place. Dendrites grew with the length of the main spine parallel to the c axis. Branching took place from the main spine at 120° intervals; this is characteristic of the threefold symmetry of tellurium. Sub-branching also took place, as can be seen in the figures. These dendrites were about 1 cm long, and the spine was about 0.05 cm in diameter. At the tip of each dendrite is a triangular pyramid. These may be formed from a small drop of liquid which clings to the dendrite as it breaks the surface of the liquid. No attempt was made to grow long dendrites.

Other dendrites were grown in the following manner. Tellurium was melted in a 50-cc Vycor crucible. The surface of the melt and the walls of the crucible were cooled slowly so that the entire exterior of the melt solidified. A seed, which had been placed in contact with the top surface of the melt before solidification, was raised until the entire solid shell surrounding the melt was withdrawn. Liquid tellurium drained through small holes in the bottom of the shell, which was then carefully broken. The crystals shown in Figure 7 were grown in this manner. This technique is similar to decantation, except that the shell has been nucleated with a single

crystal seed. The growth takes place in the form of three-dimensional crystals similar to the tips of the previously described dendrites. There is no branching, and the volume of each dendritic spine seems to indicate that the growth took place within the molten material before decantation.

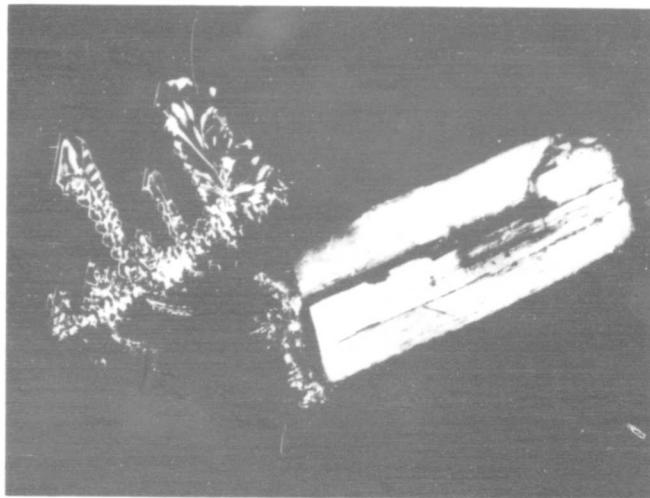


FIGURE 6. TELLURIUM DENDRITES



FIGURE 7. DENDRITIC TELLURIUM CRYSTAL GROWTH

3.6. THE CZOCHRALSKI METHOD OF PREPARING SINGLE CRYSTALS

3.6.1. EQUIPMENT. The basic Czochralski [2] apparatus is shown in Figure 8. The simplicity of this apparatus has made it an important tool for the preparation of large single crystals, not only of the elements but also of many two- and three-component compounds.

A single crystal seed is placed in the seed holder and lowered until it makes contact with the molten material contained in a suitable crucible. If the temperature of the melt is very close to the melting point of the material, a solid-liquid equilibrium can be established between the seed and the melt. Energy is removed from the solid-liquid interface and material solidified into the seed. The seed is raised slowly and the solidified material may form a single crystal, epitaxially grown from the seed.

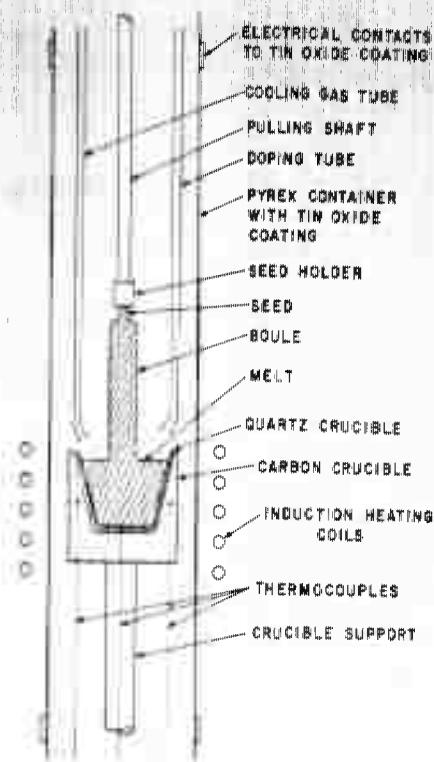


FIGURE 8. SCHEMATIC OF CZOCHRALSKI CRYSTAL-PULLING APPARATUS

Figure 9 shows the equipment used in this laboratory for the preparation of single crystals by the Czochralski technique.

The container has an OD of 90 mm, is 18 inches long, and has a wall thickness of 2 mm. Either Vycor or Pyrex tubes may be used. For growing tellurium crystals, a Pyrex tube with a

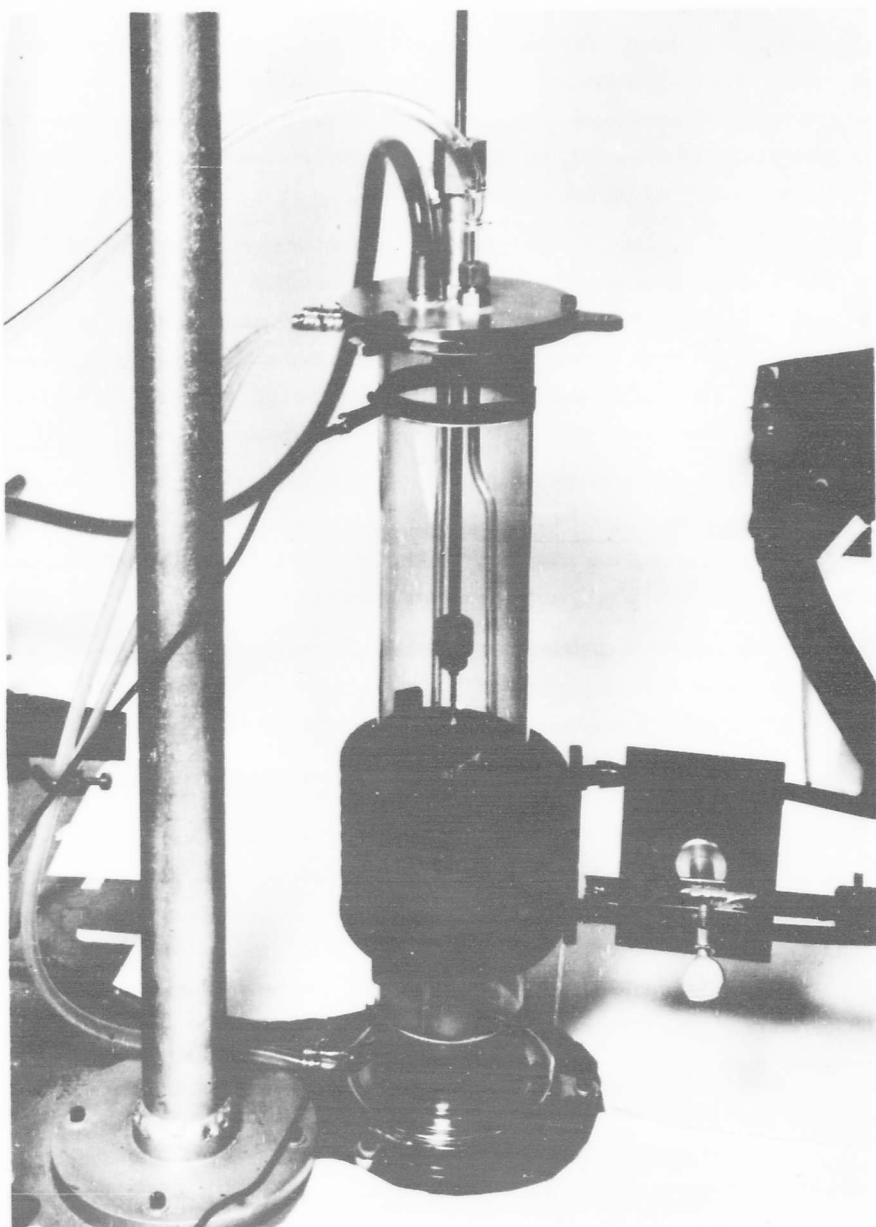


FIGURE 9. CZOCHRALSKI CRYSTAL GROWTH APPARATUS

transparent conducting coating of tin oxide was obtained from the Corning Corporation. This coating is used as a heater. The power supply is a 110-v a-c Sorensen voltage regulator and an 8-amp Variac variable transformer. The temperature of the wall of the crystal-pulling chamber can be varied between room temperature and 400°C with this equipment. The transparent heater prevents sublimation onto the tube and also provides a means for controlling the temperature gradients within the pulling apparatus.

The high-purity carbon crucible (type CCH) was obtained from the National Carbon Company. It is 46 mm by 66 mm in diameter. A cavity was milled in this cylinder for a 50-ml tapered quartz crucible; this crucible is 36 mm high and 56 mm in diameter at the top. The crucible support is 1-inch, thin-walled, stainless steel tubing. The cooling gas tube and doping tube are quartz. The pulling shaft is 0.25-inch stainless steel. The pulling rate and the rotational rate of the seed can be varied continuously and independently.

Several types of seed holders are used. The simplest seed holder is a platinum wire looped around the seed. A Jacobs chuck is also used; however, this type of holder deforms the seed. It was found that if a long seed (usually one inch in length) is used, this deformation does not interfere with crystal growth or crystal perfection.

Both ends of the Pyrex container are attached with epoxy resin to water-cooled steel flanges. Steel caps are bolted to these flanges. "O" ring seals between the cap and the flange provide a vacuum-tight system. The pulling rod is guided through the top cap by a modified "O" ring seal. The steel caps and flanges are chrome plated.

3.6.2. TEMPERATURE CONTROL. The melt is rf heated. Power is supplied by a model 0-9-J Ecco rf generator rated at 8 kva. The melt temperature is controlled by a Minneapolis-Honeywell electronic strip chart proportional controller [14]. An iron-constantan thermocouple with an ice-water reference junction is used as the temperature-sensing device. This thermocouple is imbedded in a hole drilled in the carbon crucible (see Figure 8). This system permits the temperature of the carbon crucible to be controlled to $\pm 0.1^\circ\text{C}$. Under ideal conditions, the temperature fluctuations are held to $\pm 0.03^\circ\text{C}$.

In order to grow single crystals of uniform diameter, it was found that the temperature fluctuations must be less than $\pm 0.1^\circ\text{C}$. The crystal shown in Figure 1 was grown with temperature fluctuations of less than $\pm 0.05^\circ\text{C}$. Abrupt "steps" on a crystal are the result of changes by the operator. If the operator purposely lowers the temperature 0.2°C , the result is an abrupt change in the diameter of the crystal. Figure 10 shows "steps" on several crystals which were caused by this procedure.

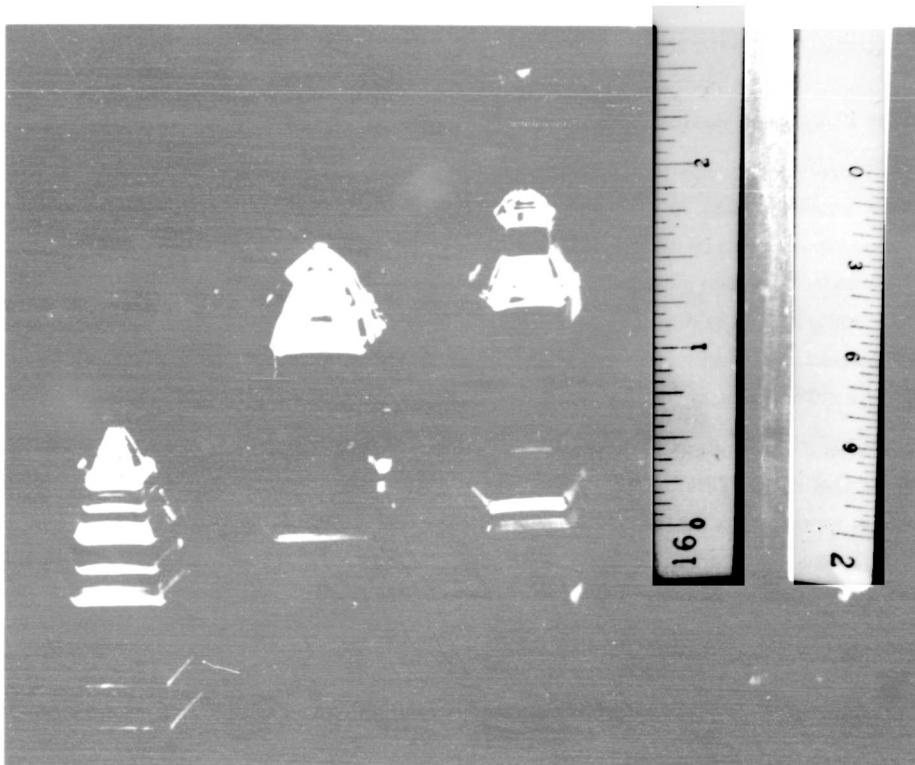


FIGURE 10. CZOCHRALSKI-GROWN TELLURIUM CRYSTALS

The liquid-solid interface during outward growth is convex toward the liquid. This was determined by manually withdrawing the crystal from the melt during outward growth.

If the temperature of the melt is increased by 0.2°C , the crystal will decrease in diameter or lose contact with the melt. Contact with the melt is not lost immediately, however. Instead, the solid-liquid interface is raised above the melt until surface tension can no longer support the liquid meniscus. In this case, the interface was found to be concave toward the liquid.

The shape of the solid-liquid interface during constant-diameter growth was not determined. For most of the crystals grown in this laboratory, it is assumed that the solid-liquid interface was continuously changing from convex to concave.

3.6.3. COOLING GAS. It was necessary to cool the surface of the growing crystal with hydrogen gas. Electrolytic hydrogen is used after being purified by passing the gas through a "Deoxo" catalytic hydrogen purifier, then a 25-mm tube four feet in length, filled with hot copper filings, and finally, a liquid-nitrogen cold trap.

Figure 8 shows how the hydrogen is used in the pulling apparatus. A 0.25-inch OD quartz tube is positioned so that the stream of hydrogen is directed toward the solid-liquid interface. Various positions were used to grow crystals. The best arrangement is that in which the gas exit is about 0.25 inch away from the growing crystal. This allows the gas to cool the center of the melt during the seeding operation. The top of the crystal is being cooled during the initial outward growth. A transition takes place as the crystal is pulled higher than the gas tube exit. The sides of the crystal are cooled after it is about 0.25 inch long.

Various types of gas tube were used. For instance, a stainless steel tube with a ring on the end was used. This tube had ten small holes evenly spaced within the ring so that the cooling gas was more evenly distributed around the growing crystal. Although this tube worked satisfactorily, the small holes had a tendency to plug up with vapor-deposited material. Another system used two separate gas flow tubes, one about 1/8 inch above the melt and the other about 3/8 inch above the melt. The lower tube was used during the initial growth, the upper one after the crystal was about 0.5 inch in length. This arrangement provided great versatility in the operation but also made the operation more complicated. No pronounced advantages of this system were observed.

A precision needle valve with a micrometer adjustment is used to control the gas flow rate. A calibrated flow gauge is used to observe the gas flow rate. The gas flow rate was about one liter per minute, but both higher and lower flow rates could be tolerated by changing the melt temperature or the ambient heater temperature.

3.6.4. SEED ORIENTATION. The normal pulling direction for tellurium is along the c axis. No attempts were made to grow crystals in other directions. The seeds were regular triangular prisms which were cleaved from larger boules. The Jacobs chuck seed holder and the natural cleavage faces provided excellent seed orientation.

It was found that misorientation of the seed by more than 1° resulted in radially asymmetrical single crystals. With a misoriented seed, one face of the crystal would grow more rapidly than the other faces. Eventually, this caused unstable growth and the crystal growth process terminated.

Seed single crystals, less than 0.25 inch in diameter and less than one inch long, could be grown even if the seed was misoriented by several degrees.

3.6.5. INITIAL GROWTH. The initial contact of the seed with the melt is made after the melt has been preheated at 455°C for one hour. During this time the seed is rotating about 0.25 inch above the melt, and the cooling gas is flowing on both the seed and the center of the apparatus.

The rf power is decreased so that the melt is cooling toward a temperature slightly above the melting point of tellurium. The seed is lowered about 1/8 inch into the melt. The tip of the seed melts and a meniscus forms above the melt. If the temperature is too high, the seed will lose contact from the melt and must be redipped. If the melt is too cold the temperature of the melt must be increased until a meniscus is formed. Under ideal conditions the meniscus will melt down to a diameter smaller than the seed and can be held in this position for ten or twenty minutes.

The seed is slowly raised and a solid "seed" will form. The extension of the seed is usually much smaller than the original seed. The best results are obtained when this extension is at least 0.5 inch long.

After the extension has been grown, the melt temperature is lowered and the top of the single crystal boule is formed. In most of our runs, all variables except the melt temperature are held constant. The outward growth is therefore dependent on the rate at which the melt temperature is lowered.

The outward growth can be stopped abruptly by increasing the melt temperature. The crystal will then stop growing outward. If the temperature is too high the crystal diameter will eventually decrease. Instead of increasing the melt temperature at this point, and therefore stopping the outward growth, the crystal can be allowed to come to a "natural" equilibrium diameter.

In either case, the melt temperature must be adjusted if one desires a crystal with a constant diameter. This is due to the fact that the level of the melt is dropping and the crystal is increasing in length during the pulling operation.

3.6.6. SEED ROTATION. Small temperature gradients in the melt and in the pulling apparatus cause the crystal to have a tendency to grow toward the cooler regions. In order to encourage symmetrical growth, the seed, the crucible, or both are rotated. In our apparatus only the seed is rotated.

It was found that as the rotational speed was increased, the tellurium crystals became more circular in cross section. That is to say, the corners of the hexagonal cross section rounded off as the rotational speed was increased. Below three rpm the crystal has sharp corners. From three to ten rpm the corners are rounded but the crystal still has distinct faces. Above ten rpm (the exact speed depends on the crystal diameter) eddy currents develop around the crystal. These eddy currents cause the crystal faces to become non-planar and distorted. Usually, a single eddy is formed behind each of the six leading edges of the rotating crystal. As the rotational speed is increased, the fluid flow around the crystal becomes more complicated. At about 20 rpm, the eddies no longer travel with the crystal.

The above discussion is for a typical 0.5-inch diameter crystal. For small diameter crystals, laminar flow is observed for the rotational speeds available, whereas for larger diameter boules, the transition from laminar to turbulent flow around the crystal occurs at lower rotational speeds. It was found that more stable growth conditions were obtained when the rotational speed was low, so that no eddies were present.

As the length of the crystal increases, the diameter will slowly decrease unless some adjustment is made in the operating conditions. It was found that by decreasing the temperature of the melt slowly, a crystal with uniform diameter could be produced. The temperature of the carbon crucible was decreased in a stepwise manner, about 0.05°C every ten minutes. This was at the discretion of the operator. During one run, the temperature was held constant ($\pm 0.03^{\circ}\text{C}$) for two hours with only a 1 mm decrease in diameter over a one-inch length. Any change in other parameters, such as the gas flow or drafts across the pulling apparatus, can force the operator to vary the crucible temperature in an erratic manner. This will result in a crystal with abrupt changes in the diameter.

The crystal growth is usually terminated by increasing the temperature of the melt and increasing the pulling rate. The crystal will usually decrease in diameter slightly and then break contact with the melt. A small drop of liquid will usually cling to the bottom of the boule. This can result in the crystal being deformed in the region around the droplet.

In order to eliminate this, many of the crystals were slowly "necked down" to a small diameter (usually less than 1/8 inch). Then a small crystal, similar to the seed, was grown before breaking contact with the melt. The small drop of liquid which clings to this section will not deform the large single-crystal boule.

3.6.7. POLYCRYSTALLINE GROWTH. For tellurium, as well as other materials, most polycrystalline boules are the result of either an imperfect seed or a poor weld when initial

contact is made between the seed and the melt. After a good weld has been made, the diameter of the boule can increase or decrease without introducing new crystals. However, if the diameter increases too rapidly, dendritic growth will take place at the corners of the hexagonal boule. Usually the growth at three of the corners will proceed at the expense of the growth at the faces of the boule. Eventually, a triangular boule with concave faces will form.

If the dendritic growth occurs when the diameter of the boule is small, the faces will "fill in" and a hexagonal boule will form. This always results in polycrystalline material. The cross section of the boule will be a regular hexagon. Very fine lines will appear on the faces of the boule. Small bumps may appear and the boule will develop new faces if the growth is continued for several hours. The stability of growth improves once the boule becomes polycrystalline. That is, it is relatively easy to grow a uniform diameter polycrystalline boule of tellurium.

Bi-crystals of tellurium resulted in the following way. Small crystals of tellurium form in the vapor above the melt. The reflection of light from the faces of these crystallites may be observed during growth. Most of these crystallites apparently fall back into the melt and do not interfere with growth. Occasionally a crystallite will reach the solid-liquid interface at the circumference of the boule and attach itself onto the crystal. The boule then becomes a bi-crystal. The crystallite may "grow itself out" if this occurs during the outward growth of the boule. It was standard practice to discontinue the growth of any boule in which a surface blemish occurred.

3.6.8. REDIPPING. A boule one inch in length and 0.5 inch in diameter was extracted from the melt. The boule was then lowered into the melt. The melt temperature was increased in order to melt about 1/8 of an inch from the length of the boule. The temperature was again lowered and growth was continued until the crystal was two inches in length. The diameter of the boule was increased about 1/16 inch at the new weld. The crystal was cleaved at room temperature (see Section 4). Perfect cleavage was obtained across the new weld. No sign of polycrystalline material was observed. Various etches (see Section 4) did not reveal the re-weld boundary.

Several other attempts were made to establish a weld on a large diameter crystal. One boundary revealed small bubbles. In another crystal a large bubble was found at the boundary. It is concluded that if a large crystal is redipped, the boule must be melted back and held at a high temperature until any entrapped gasses are eliminated from the interface.

3.6.9. THE EFFECT OF IMPURITIES ON GROWTH. Single crystals of tellurium were grown from a melt containing selenium or silver. One percent by weight of the impurity was introduced

into the molten tellurium through the doping tube. In the case of selenium, considerable vaporization of the impurity occurred.

For both selenium and silver, a remarkable change in the growth process was observed. The pulling rate had to be decreased from the usual 0.25- to 0.5-inch per hour rate to 1/8 inch per hour. It was not possible to grow a single crystal boule larger than 0.25 inch in diameter. With selenium, the boule faces became very planar and the corners sharp. The growth temperature was higher than normal even though selenium lowers the melting point of tellurium.

The single crystals with selenium as an impurity were darker and more brittle than pure tellurium. The silver-doped crystals cleaved and had the same appearance as pure tellurium. Electrical measurements indicated that both selenium and silver had been incorporated into the tellurium crystal.

4 FABRICATION

Once the crystal is grown, there remains the rather difficult problem of preparing a sample for use in optical or electrical measurements.

4.1. SHAPING

Slabs may be extracted from a tellurium boule by cleaving or fracturing, sawing, etching, or sand blasting.

Tellurium has perfect cleavage parallel to any face of the hexagonal prism. The material will fracture along any other plane parallel to the c-axis. Fracture also occurs perpendicular to the c-axis. No other cleavage or fracture planes have been found.

Large area slabs of tellurium 2 mm thick have been cut with mechanical saws. Tellurium slabs as thin as 1 mm have been prepared by an acid string saw which had a platinum string, CP4-A was used as the acid. Large area slabs have been prepared by sand-blasting; however, it is difficult to make an even cut over a large area. Ultrasonic grinding has been used with poor results. The sample usually splinters along cleavage planes. Once a slab has been extracted, either sand-blasting or etching can be used to form intricate shapes.

All of the mechanical techniques mentioned above introduce imperfections into the crystal. It is therefore desirable that etching techniques be used if possible. Cleaving and fracturing should be performed at low temperatures.

4.2. ETCHING

After the sample is shaped, it is desirable to remove the badly strained outer layer of tellurium. A chemical polish consisting of one part chromic anhydride, one part concentrated hydrochloric acid, and three parts water by weight removes about $4\mu/\text{min}$.⁵ Hot concentrated sulfuric acid may also be used.

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P. O. Box 618
Ann Arbor, Michigan

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DESCRIPTORS**

Crystals
Crystal Growth
Crystal Structure
Crystallography
Single Crystals
Recrystallization

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**UNCLASSIFIED
INSTRUCTIONS**

CORRECT
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Ref. 25/9
Title: Project MICHIGAN
Project No.: 3070000000

I. Title: Project MICHIGAN
II. Researcher: Richard C. Kassner,
III. U. S. Army Electronics
Command
IV. Contract DA-30-1009
SC-1000
V. Project No.: 3070000000
VI. Description: The investigation concerned the preparation of single crystal
silicium carbide by the slow-cooling, vapor, hydrocarbon, and
Czochralski methods and determined the best method to
be employed. The Czochralski method has provided larger
(17 mm diameter by 10 mm long) single crystal boules,
and looks well to the utilization of diamond as a heating element
material. The results obtained are available in the report
submitted by Bell Telephone Laboratories. The use of
epoxy technique for fabrication of silicon carbide
and electrical insulation.

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